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(54) Dental restorative compositions having improved mechanical properties and hydrolytic stability.

(57) There is disclosed a dental restorative composition containing a hydrophobic polymerizable composition, a polymerization initiator, and a quartz or heat treated barium or strontium glass hydrophobic filler having an average particle size below 15 microns, with said filler being present in an amount within the range of from about 35 to about 78 volume per cent.

DENTAL RESTORATIVE COMPOSITIONS HAVING IMPROVED MECHANICAL
PROPERTIES AND HYDROLYTIC STABILITY

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10 The invention relates to a dental restorative composition
having improved mechanical properties and hydrolytic
stability.

Background of the Invention

15 Dental restorative compositions comprising a polymerizable
resinous composition plus a filler are finding wide accep-
tance in the practice of dentistry. An illustration of
such compositions is the dental filling material described
by Lee et al. in U.S. Patent No. 3,539,533. However, such
20 resin based dental filling materials have found limited
use for the filling of cavities on the grinding surfaces
of molars. The reason for this is that such compositions
have been found to have inadequate wearing properties to
withstand the stresses which are normal in such areas.
25 Among the factors that contribute to the inadequate wear
properties of the prior art resinous dental restorative
dental compositions are microfractures of the overall
composite and debonding that occurs at the filler/polymer
matrix interface. Both of these are most likely to occur
30 during the cyclic loads encountered while chewing in an
aqueous environment, with modest temperature fluctuations.
Inadequate hydrolytic stability appears to contribute to
both the microfractures and debonding. The present
invention is directed to a dental restorative composition
35 that substantially improves hydrolytic stability,

resistance to debonding at the filler/polymer interface, and resistance to the formation and propagation of microfractures in the composite.

5 Brief Summary of the Invention

The invention provides a dental restorative dental composition that consists essentially of the following three components:

10

(a) a polymerizable composition containing at least one compound having at least two olefinically unsaturated groups, wherein, when said polymerizable composition is polymerized in the unfilled state, the resulting cured material has a water absorption as determined by ADA Specification No. 27 at 37°C. for one week, of less than 1 milligram per square centimeter;

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(b) a polymerization initiator for said polymerizable composition; and

20

25

(c) a particular hydrophobic inorganic filler having at least 30 per cent of the particles and preferably at least 70 to 100 per cent of the particles less than 5 microns, with a corresponding volume average particle size not more than 15 microns and preferably not more than 5 microns, said filler being present in an amount within the range of from about 35 to about 78 volume per cent, based on volume of said polymerizable composition plus said filler.

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In a preferred aspect, the composition of the invention contains from about 5 to about 30 weight per cent of colloidal silica, the percentage being based upon the weight of the entire dental restorative composition.

The Prior Art

- 5 Dental restorative compositions that include a polymerizable resinous compound free of active hydrogen have been disclosed. For instance, see Orłowski et al., U.S. Patent No. 4,220,582, who disclose the use of the dimethacrylate of ethoxylated bisphenol-A and polyethylene glycol dimethacrylate in dental restorative compositions.
- 10 The use in dental restorative compositions of hydrophobic fillers such as quartz has been disclosed. For instance, see Schmitt et al. in U.S. Patent No. 3,923,740.
- 15 Ibsen et al., in U.S. Patent No. 4,297,266, disclose dental restorative compositions containing "hydrophobic" colloidal silica and 2 to 30 micron glass particles as fillers. Among the resins disclosed are ethoxylated bisphenol-A dimethacrylate and triethylene glycol dimethacrylate.
- 20 Dixon, in U.S. Patent No. 4,222,835, teaches polymerizable compositions (for coatings or fiber glass-reinforced materials) containing a wide variety of acrylic esters.
- 25 Lee et al., in U.S. Patent No. 4,032,504, disclose dental restorative compositions including a filler having a particle size of from 0.5 to about 50 microns, with an average particle size of from about 2 to about 15 microns.
- 30 Ibsen et al., in U.S. Patent No. 4,297,266, disclosed dental restorative compositions containing glass particles and a hydrophobic silica filler.

Rossi, in U.S. Patent No. 3,792,531, contains a similar disclosure. Dental restorative compositions containing sub-micron size fillers have also been disclosed. For instance, see Australian Patent No. 484,167.

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Detailed Description of the Invention

In its broadest aspect, the invention provides a means to obtain a combination of a number of desirable features.

10 First, the polymerizable compositions employed in the invention are relatively hydrophobic when cured, which enhances the hydrolytic stability of the restorative compositions. Second, relatively hydrophobic and chemically durable fillers are employed in order to
15 provide additional resistance to hydrolytic attack at the filler/polymer matrix interface. And third, the use of small filler particles at relatively high filler loadings decreases the interparticle spacing in the cured composite which results in an increased number of obstacles to the
20 propagation of small cracks initiated by defects in the system such as voids. In preferred aspects of the invention, the number of voids in the cured composite are reduced by employing relatively low viscosity resinous compounds, and/or by mixing the paste system under vacuum
25 and preserving the resultant low void content by the use of a single component photocured system.

The various components of the invention, which are described more fully below, are employed for the purpose
30 of achieving the above described features of the invention.

The polymerizable composition that is employed as the polymer matrix in the invention is a compound that has at
35 least two olefinically unsaturated groups and which is relatively hydrophobic when cured, as is evidenced by low

water absorption. One way to obtain the desired hydrophobic properties is to employ polymerizable compounds that are free of active hydrogen. By "active hydrogen" is meant the hydrogen contained in groups such as hydroxyl, carboxyl, primary or secondary amino, amido, sulfhydryl, and the like. (A convenient test for such active hydrogen groups is that they react with isocyanate in the presence of tertiary amine catalyst.) A wide variety of such compounds can be employed. They include alkoxylated bisphenol-A acrylates or methacrylates, alkane diol acrylates or methacrylates, polyalkylene glycol acrylates or methacrylates, and the like. The preferred compounds are the $C_4 - C_{12}$ alkane diol acrylates or methacrylates such as 1,10 decamethylene diol dimethacrylate and 1,6-hexamethylene diol dimethacrylate, and ethoxylated bisphenol-A dimethacrylate. The nature and preparation of such compounds are known in the art.

The dental restorative composition of the invention includes a polymerization initiator. Such initiators are known in the art and can be used in their customary proportions. For instance, the composition can be divided, one package containing a peroxide such as benzoyl peroxide, and the other containing an activator for the peroxide such as N,N-di-(2-hydroxyethyl)-p-toluidene. Other initiator systems known in the art can also being used.

In order to minimize the formation of voids, in a preferred aspect of the invention, the initiator is a photosensitive initiator system so that the mixing step necessary for the two-component, self-curing composite systems can be avoided. In this aspect, a one-package system is used. Resin, filler, and the photosensitive initiator system are mixed under a vacuum to reduce void formation. The composition then needs no further mixing by the dentist or dental technician. Such photosensitive

initiator systems include benzoin, benzoin ethers and esters, 2,2-diethoxy acetophenone, and the diketone compounds plus a reducing agent that are disclosed by Dart et al., in U.S. Patent No. 4,071,424. Specific examples
5 of preferred photoinitiator systems include benzil and/or camphoroquinone plus N,N-dimethylaminoethyl methacrylate or ethyl 4-(N,N-dimethylamino-)-benzoate.

The filler employed in the invention has a volume average
10 particle size below 15 microns, and preferably, below 5 microns. Thirty per cent of the filler particles, and preferably 70 to 100 per cent, have a size below 5 microns. The filler is employed in an amount within the
15 range of from about 35 to about 78 volume per cent, based on the volume of the filler plus the polymerizable composition. Thus, the filler is employed in relatively high proportions. A volume per cent of 35 to 78
corresponds approximately to 50 to 95 weight per cent of the dental restorative composition of the invention,
20 depending on the specific gravity of the filler.

The hydrophobic, chemically durable fillers that are used are quartz and/or a particular heat-treated barium or strontium glass. The hydrophobic fillers will absorb less
25 than 0.1 weight per cent water (prior to addition of silane coupling agent) when exposed to normal ambient conditions. Water content of the filler is determined by a differential scanning calorimeter ("DSC"). The first departure from baseline in a DSC scan is caused by the
30 presence of water. To determine the amount present, the area under the peak is determined and normalized relative to the weight of the sample.

The barium or strontium glass that may be employed as the filler is selected for chemical durability, as is evidenced by resistance to leaching in an aqueous environment. Such glasses are substantially free of alkali metal oxides, and are single phase glasses. If the mole per cent of barium or strontium oxide exceeds a certain point, the glass becomes two-phased. This proportion can vary, depending upon the presence and proportion of other metal oxides in the glass. For one preferred type of glass that is composed of oxides of barium, silicon, boron, and aluminum, the upper limit for a single phase glass is about 20 mole per cent barium oxide. One preferred glass for use in the invention has the following composition:

SiO_2	- 67	mole per cent
BaO	- 16.4	mole per cent
B_2O_3	- 10	mole per cent
Al_2O_3	- 6.6	mole per cent

The essential ingredients in the glass are the oxides of barium and/or strontium and silicon. Oxides of other metals such as aluminum and boron may also be present so long as such oxides do not detract from the chemical durability of the glass. Thus, significant quantities of alkali metal oxides should be avoided because, as is well known, alkali metal ions are quite soluble in aqueous media, and therefore will reduce the chemical durability of the glass. The minimum barium and/or strontium content of the glass is preferably that which is sufficient to impart x-ray opacity to the glass.

The barium and/or strontium glass powder used in the invention is acid washed and then subjected to a heat treatment to enhance its resistance to attack by water. The procedures are the following:

5

The acid-washing treatment to which the glass powder is subjected is carried out by known procedures. For instance, a mixture of 1 part (by weight) of glass powder, 1 part of 37 per cent aqueous hydrochloric acid, and 10 1 part of de-ionized water is stirred at room temperature for 45 minutes, filtered, and rinsed with de-ionized water until the pH of the filtrate is the same as the rinse water. The powder is then dried at about 50°C. overnight in a forced air oven. The acid wash is used to remove 15 metal impurities from the glass, and to reduce the amount of leachable barium or strontium from the surface of the glass.

20

The acid-washed glass powder is subjected to a heat treatment to reduce the affinity of the glass powder for water. This heat treatment is carried out at an elevated temperature below the sintering temperature of the glass powder (the sintering temperature can be determined by known procedures, as by thermo-mechanical analysis "TMA"), 25 but high enough to cause a significant reduction in the specific surface area of the glass powder, as measured by known procedures such as by a "Quantasorb" B.E.T. surface area analyzer. The reduction in specific surface area will usually be at least 50 per cent (i.e., the surface 30 area of the heat treated glass powder will be less than about one-half that of the untreated powder), up to 80 to 90 per cent, or even more in some cases. The heat treatment time is not at all critical in that it need be carried out only for the minimum time needed to heat all

the powder to the desired temperature. Apparently the effect of the heat on the glass powder is quite rapid, and all that is required is to bring all of the mass of powder up to the desired temperature. However, since the glass powder is an excellent heat insulator, this can take several hours for masses of powder wherein the heat must travel through a significant thickness of powder to heat all of the glass to the desired temperature.

The following is an illustration of a preferred heat treatment carried out on the barium glass used below in the Examples, and referred to as Filler A or Filler B:

The barium glass had the following composition:

SiO ₂	-	67	mole per cent
BaO	-	16.4	mole per cent
B ₂ O ₃	-	10	mole per cent
Al ₂ O ₃	-	6.6	mole per cent

The raw glass powder, prior to acid wash, has a specific surface area of about 0.8 ± 0.1 m²/gm. After acid-washing as described above, the specific surface area is about 10 ± 2 m²/gm.

Five kilograms of the acid-washed powder are placed in a saggar crucible. The crucible is cylindrical, about 12 inches in diameter and 10 inches high. Five kilograms of the powder nearly fill the crucible. The crucible containing the powder is placed in an oven, which is set at 650°C. It takes about 16 hours for the entire mass of powder to heat up to 650°C. After 16 hours, the furnace is turned off and the powder is slowly cooled to room temperature. The specific surface area of the heat treated glass is about 3.5 ± 1 m²/gm.

As is known in the art, a silane coupling agent can be employed to enhance the bond between the filler and the resin. Such coupling agents include gamma-methacryloxy-propyltrimethoxysilane.

5

It is desirable to include a small percentage of colloidal silica in the composition in order to adjust the viscosity and the handling characteristics of the composite paste. For instance, from about 2 to about 25 weight per cent of colloidal silica, based on weight of the entire composite, is beneficial.

10

The colloidal silica is preferably treated with a silane coupling agent such as gamma-methacryloxypropyl-trimethoxysilicone ("A-174"). After such treatment, the silica should be protected from ambient moisture because it may absorb up to about 1 weight per cent of water from the atmosphere, as measured by DSC.

15

In the examples, the following materials were used:

20

Bisphenol-A dimethacrylate ("BADM")

Ethoxylated bisphenol-A dimethacrylate ("EBDM")

25

Methacrylic acid ("MAA")

1,6-hexamethylene glycol dimethacrylate ("HMGDM")

30

2,2'-propane bis[3-(4-phenoxy)-2-hydroxypropyl-1-methacrylate] ("Bis-GMA")

Tetraethylene glycol dimethacrylate ("TEGDM")

2-(N,N-dimethylamino)ethyl methacrylate ("DMAEMA")

Ethyl 4-(N,N-dimethylamino)benzoate ("EDMAB")

- 5 Filler A - Conventional acid-washed 0-13 μ barium glass powder having the following particle size analysis (by Coulter Counter):

10 100% below 13 μ
55% below 5 μ
18% below 2 μ

Water content, by DSC, was 1.05 weight per cent

- 15 Filler B - Same 0-13 μ glass powder as Filler A, but heated to 650°C. for sixteen hours as described above. The water content, by DSC, was 0.05 weight per cent..

- 20 Filler C - Quartz powder (0-90 μ) having the following particle size analysis:

100% below 80-100 μ
50% below 13 μ
16% below 5 μ

25

The water content, by DSC, is below 0.01 weight per cent.

Filler D - Quartz powder (0-10 μ) having the following particle size analysis:

30

100% below 10 μ
77% below 5 μ
23% below 2 μ

- 35 Water content, by DSC, is below 0.01 weight per cent.

Filler E - 0-90 μ Barium glass powder heat treated at 650°C. for 16 hours, having the following particle size analysis:

5 100% below 80-100 μ
 50% below 13 μ
 12% below 5 μ

Water content, by DSC, is 0.025 weight per cent.

10

Filler F - 0-5 μ Quartz powder having the following particle size analysis:

15 100% below 5 μ
 70% below 1 μ
 Average - 0.66 μ

Water content, by DSC, was 0.01 weight per cent.

20 The water contents are determined on the fillers prior to treatment with silane. The quartz fillers were treated with 3.2 weight per cent A-174 silane (Union Carbide), and the barium glass fillers were treated with 1 weight per cent A-174 silane (gamma-methacryloxypropyl-trimethoxy-silane).

25

Examples 1-2 and Controls 1-3

30 A series of filled resin systems, formulated to be useful as dental composites, were prepared. The composite formulations were prepared by mixing fillers into the resins using a mini-Hobart (drill) mixer until a smooth paste resulted. The pastes were then placed in a vacuum

35 oven and de-gassed at about 4 mm. mercury pressure until

they were void-free, as determined by microscopic examination. Flexural test samples were made by placing the uncured filled resins in "Teflon" molds between glass slides, and exposing each side to 60 seconds exposure from a 75 watt/12 volt quartz projector lamp. All samples were aged for 24 hours at 37°C. in deionized water. Ten samples of each composite were tested for initial flexural strength, and ten additional samples were placed in pressure bottles with 300 ml. of deionized water, and were held at about 5 atmospheres and 145°C. for 7 days. After this time, they were removed from the bottles and tested for flexural strength, using an Instron HP-11 stress-strain testing apparatus.

Table I displays the formulations and Table II displays the results of the flexural testing.

Table I

20	<u>Resin A</u>	<u>Parts by weight</u>
	Bis-GMA	61.2
	BADM	6.8
	TEGDM	26.9
	MAA	2.0
25	Benzil	0.3
	Camphorquinone	0.3
	DMAEMA	2.5
	Viscosity - 2560 cps	
	Water Absorption(1) - 2.34 mg/cm ² (0.01)(2)	
30	<u>Resin B</u>	
	EBDM	96.9
	Camphorquinone	0.3
	Benzil	0.3
35	DMAEMA	2.5
	Viscosity - 2240 cps	
	Water Absorption - 0.41 mg/cm ² (0.01)	

Resin C

	EBDM	84.55
	HMGDM	12.6
	Camphorquinone	0.25
5	DMAEMA	2.5

Viscosity - 1960 cps

Water Absorption - 0.80 mg/cm²

-
- 10 (1) The water absorption was determined on the cured,
unfilled resins by ADA Specification No. 27 -
immersion in water at 37°C. for seven days.
- (2) The numbers in parentheses after the test data are
15 the standard deviations.
-

Control 1

	Resin A	28
20	Filler A	72

Control 2

	Resin A	28
	Filler B	72

25

Control 3

	Resin B	28
	Filler A	72

30

Example 1

	Resin B	28
	Filler B	72

Example 2

35	Resin C	28
	Filler B	72

Table II

<u>Flexural Strength</u>				
Composite	Initial Strength (N/mm ²)	Pressure Boiled 7 days	% Loss	Water
				Absorption ⁽³⁾ mg/cm ² , 7 days at 37°C.
Control 1				
(hydrophilic resin)	111.0	30.4	72.6	1.23
(hydrophilic filler)	(13.4)	(7.9)		(0.03)
Control 2				
(hydrophilic resin)	108.3	46.4	56.2	1.07
(hydrophobic filler)	(10.6)	(8.9)		(0.03)
Control 3				
(hydrophobic resin)	109.6	66.7	39.1	0.44
(hydrophilic filler)	(13.7)	(9.9)		(0.03)
Example 1				
(hydrophobic resin)	111.6	78.6	29.6	0.29
(hydrophobic filler)	(10.7)	(9.9)		(0.02)
Example 2				
(hydrophobic resin)	109.2	91.4	16.3	---
(hydrophobic filler)	(13.2)	(9.2)		

(3) Water absorption on the filled composites.				

Controls 1, 2, and 3, each of which contained either a hydrophilic resin or a hydrophilic filler or both, had much lower retention of flexural strength after pressure boiling, than did Examples 1 and 2, which exemplify the invention.

Example 3

To illustrate the effect of particle size, 28 parts, by weight, of Resin B was mixed with 72 parts of Fillers C, D, E, and B, respectively. The composites were vacuum de-gassed and made into flexural test samples, as was described in Example 1. The flexural strengths were determined after aging for 24 hours in deionized water at 37°C. The results are displayed in Table III:

Table IIIFlexural Strength

<u>Filler</u>	<u>N/mm²</u>
C (0-90 μ quartz)	117.4 (8.7)
D (0-10 μ quartz)	124.3 (11.7)
E (0-90 μ Ba glass)	108.1 (7.3)
B (0-13 μ Ba glass)	119.1 (7.7)

Examples 4 and 5

Two photocurable compositions designed for use as dental composites were made from the following formulations (Table IV):

Table IV

<u>Example 4</u>	<u>Parts, by Weight</u>
Resin B	22.2
Filler D	66.8
Colloidal Silica(4)	11.0
<u>Example 5</u>	
Resin B	21.6
Filler B	67.5
Colloidal Silica(4)	10.9

(4) Fumed silica treated with gamma-methacryloxypropyl trimethoxysilane. (Cab-O-Sil "M-5", Cabot Corporation)

The compositions were vacuum degassed and cured by exposure to light, as described in Example 1.

Representative properties of these materials after curing as described in Example 1 are shown in Table V:

Table V

	<u>Example</u>	
	<u>4</u>	<u>5</u>
Compressive Strength, N/mm ²	354.1	357.7
Diametral Tensile Strength, N/mm ²	64.9	61.4
Flexural Modulus, N/mm ²	10,956	9,650
Flexural Strength, N/mm ²	126.1	127.9
Rockwell F Hardness	93	94
Water Absorption, %	0.38	0.32
Translucency	passes ADA spec 27	
Flexural Strength, N/mm ² , after pressure boiling 7 days at 145°C. and 5 atmospheres	86 (32% loss)	117 (8% loss)

To demonstrate the benefit of vacuum degassing to reduce voids, samples of the same formulations were cured without having been vacuum degassed, and were tested for flexural strength as described above in Example 1. The results were:

Example 4	99.5 N/mm ²
Example 5	90.8 N/mm ²

EXAMPLE 6

The following dental composite formulation was prepared:

TABLE VI

	<u>COMPONENT</u>	<u>PARTS, BY WEIGHT</u>
5	EBDM	17.71
	dl-camphoroquinone	0.05
	Benzil	0.024
	EDMAB	0.216
	Resin	18.000
10	Filler F	62
	Colloidal Silica ⁽⁵⁾	20

(5) "OX-50", marketed by DeGussa; It is a fumed silica having a surface area of 50 m²/gm and an average particle size of 0.05 μ . It is treated with 10 weight per cent A-174 silane and has a water absorption content, by DSC, after such treatment of 0.7-0.8 weight per cent.

20 The composite was prepared by the following procedure:

The resin is charged to a Hobart mixer, and the quartz and silica are added in six equal portions, with mixing, over a period 1-1/2 hours. The mixture is then charged to a double planetary mixer, which is kept at an absolute pressure of 65 millimeters of mercury. The agitators in this mixer are run for about 20 seconds every 15 minutes; the mixture is kept in the mixer for 1-1/4 hours.

30 Samples were cured by exposure to light, as described in Example 1. The following physical properties were measured on the cured composite:

TABLE VII

	Compressive Strength, N/mm ²	340	(49,000 psi)
	Diametral Tensile Strength, N/mm ²	67.6	(9,880 psi)
5	Flexural Modulus, N/mm ²	17,500	
	Flexural Strength, N/mm ²	134	
	Rockwell F Hardness	101.2	
	Translucency	Passes ADA SPEC 27	

- 10 In a dental composite, one of the important physical properties that has an effect on durability is flexural modulus. The flexural modulus of natural tooth enamel is of the order of 50,000 to 80,000 N/mm². Where there is a large difference between the flexural moduli of natural
- 15 enamel and the restoration, significant stresses can be encountered at the enamel/restoration interface.

- One of the reasons that polymer-based dental composites may not function well in Class 2 restorations (i.e., on
- 20 biting surfaces of molars) is the large disparity between their flexural moduli (which can be as low as 7000 N/mm²) and that of natural tooth enamel. While the inventor herein has observed isolated batches of conventional composite material whose flexural moduli have approached
- 25 that of this Example 6, preferred embodiments of the restorative compositions of this invention are the first composite formulations that the inventor has seen whose properties, including flexural modulus, are consistently such that they are legitimate candidates for clinical
- 30 evaluation as Class 2 restorative materials.

CLAIMS:

1. A dental restorative composition consisting essentially of:

5

(a) a polymerizable composition containing at least one compound having at least two olefinically unsaturated groups, wherein, when said polymerizable composition is polymerized in the unfilled state, the resulting cured material has a water absorption as determined by ADA Specification No. 27 at 37°C. for one week, of less than 1 milligram per square centimeter;

10

(b) a polymerization initiator for said polymerizable composition; and

15

(c) a hydrophobic inorganic filler having a volume average particle size below 15 microns, at least 30 per cent of the particles of said filler having a size of less than 5 microns, said filler being present in an amount within the range of from about 35 to about 78 volume per cent, based on weight of said polymerizable composition plus said filler, and said filler being selected from the group consisting of quartz and heat treated barium or strontium glass.

20

25

2. The dental restorative composition of claim 1 wherein said component (a) is at least one compound selected from the group consisting of $C_4 - C_{12}$ alkanediol acrylate or methacrylate and alkoxyated bisphenol-A acrylate or methacrylate.

30

3. The dental restorative composition of claim 1 wherein said component (a) includes ethoxylated bisphenol-A dimethacrylate.

35